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Short communication

A novel single flow zinc–bromine battery with improved energy density

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HIGHLIGHTS

- A novel single flow zinc–bromine battery (ZBB) was first proposed and fabricated.
- The battery shows improved energy density than traditional ZBB.
- The new design can effectively inhibit the bromine emission.
- The performance of single flow ZBB is comparable with traditional ZBB.

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ABSTRACT

A novel single flow zinc–bromine battery is designed and fabricated to improve the energy density of currently used zinc–bromine flow battery. In the assembled battery, liquid storage tank and pump of positive side are avoided and semi solid positive electrode is used for improving energy efficiency and inhibiting bromine diffusion into environment. The single flow battery with this design shows columbic efficiency (CE) of 92% and energy efficiency (EE) of 82% over 70 cycles at the current density of 20 mA cm^{-2}, which is comparable with the performance of the traditional zinc–bromine flow battery; furthermore, it has much lower weight and bromine emission.

1. Introduction

Redox flow batteries (RFBs) were first proposed in the early 1970s by Larry Thaller in NASA [1]. In this electrochemical energy storage system, the electric energy is stored in two separated solutions, which contain different redox couples with different electrochemical potentials. RFBs are considered as promising technologies for large-scale energy storage due to their advantages of long cycle life, low cost of maintenance, flexible design and high efficiency. So far, a number of RFB systems including Fe/Cr [1–3], all-vanadium [4–6], Zn/Br_2(ZBB) [7] and polysulfide/Br_2 [8] have been successively proposed and developed. Among them, the all-vanadium redox flow battery (VFB) uses the same element in both half-cells, which avoids the cross-contamination of the two half-cell electrolytes. However, the energy density (25–30 W h kg^{-1}) of the VFB is limited by vanadium ion solubility in the supporting electrolyte [9].

As one kind of energy storage techniques, the ZBB is well suitable for large scale stationary applications due to its higher energy density (70 W h kg^{-1}) and lower cost compared with the other candidates [10,11]. The ZBB utilizes $ZnBr_2$ as electrolyte in both anode and cathode. The electrochemical reactions of the ZBB are the cathodic deposition of zinc and the anodic formation of a polybromide phase during charging [12–15]. Even though ZBB has already shown promising application in large scale energy storage, a number of technical issues still need to be overcome. For example, the highly hazardous bromine could be easily emitted into environment; the two storage tanks together with two pumps make the system rather heavy and further lead to a low energy density. Therefore, how to improve the energy density and avoid bromine pollution have become the most important R&D topics of ZBB at present. Recently, single redox flow battery based on lead–acid battery system was proposed by Pletcher et al. [16,17]. This new system differs from traditional redox flow battery, since only a single solution was used as electrolyte, while no ion exchange membrane is needed. At the same time, the system design can be greatly simplified because the fact that only half of the battery system needs the pump and electrolyte tank. It seems that hybrid flow batteries are more suitable for the design of single flow battery, since one part of electrochemical reactions is based on dissolution and deposition. For example, Cu/PbO_2 and Zn/NiOOH

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single flow batteries were proposed by Cheng [18] and Pan [19], respectively.

Considering hybrid nature of ZBB, it is possible to use single flow battery instead of the traditional ZBB. The single flow ZBB could improve the energy density as well as inhibit bromine diffusion due to the fact that positive tank which contains the polybromide can be given up in the new design. The new system could overcome the issues which have been extremely troublesome so far for ZBB. In this paper, a novel single flow ZBB was designed to improve the energy density and inhibit bromine emission of traditional ZBB. The diagram of the novel single flow battery is proposed herein (Fig. 1). In this design, the supply system of anolyte (Br_2/Br^-) was eliminated. The carbon felt coated with active materials and complexation reagents was used as positive electrode. The complexation reagents were optimized and the performance of the battery was investigated in detail.

2. Experimental

2.1. Cyclic voltammetry (CV)

The cyclic voltammetry was carried out on a potentiostat (Model 2273, EG & GPAR) in a three-electrode cell. A piece of graphite plate (2 cm × 2 cm) and a saturated calomel electrode (SCE) were employed as counter and reference electrodes, respectively. To investigate the reversibility of the positive redox couple, a glassy carbon (GC) disk electrode ($d = 4$ mm) coated with carbon powder was used as the working electrode. It was prepared by dripping 10 μl of carbon powder ink onto the pre-polished GC disk electrode. The ink was made by dispersing 5 mg activated carbon powder and 20 μl of 0.05 wt% Nafion solution in 1.0 ml ethanol under a strong ultrasonication.

2.2. Preparation of semi solid positive electrode

A piece of carbon felt was employed as the substrate for mixing positive active material. The mixed active material layer was prepared by coating mixed active material slurry onto one surface of the carbon felt with loading about 6.0 mg cm^{-2}. This mixed active material slurry was made by dispersing 1.0 g of active carbon in 5.0 ml 6.0 M $ZnBr_2$ solution. Then the carbon felt was marinated in the prepared 6.0 M $ZnBr_2$ solution for 30 s to obtain the semi solid positive electrode.

2.3. Charge–discharge cycling test under a constant current density

The charge–discharge tests were carried out with a LAND CT 2001A battery test system (Jinnuo Wuhan Corp., China) at room temperature. The cell was first charged to 720 mA h and then discharged to 1.0 V at the constant current density. The active materials utilization of positive electrode is 44.9%. Fig. 1 shows a diagram of the single flow ZBB used for the charge–discharge cycling test under a constant current density. It employed carbon–polymer composites as current-collectors. A piece of semi solid positive electrode (with thickness of 3 mm and geometrical area of 6 × 6 cm^2) was used as the positive electrode. A plastic spacer with 3 mm of thickness was installed in the negative chamber to guarantee the sufficient space for zinc deposition and growth. Positive and negative half-cells were separated by a piece of membrane. The solution containing 2.0 M $ZnBr_2$ was used as the electrolyte stored in tank. The pump was used to flow electrolyte into negative half-cell compartment at flow rate of 16 cm s^{-1}.

3. Results and discussion

To better know the optimized membrane separators and complexes for the single flow ZBB, the batteries assembled with different membrane separators (Nafion 115, Daramic) were fabricated and tested. The battery was charged at the current density of 20 mA cm^{-2} for 60 min and then discharged at the same current density to a cut-off voltage of 1.0 V as shown in Fig. 2. It was observed that the average charge (discharge) voltage of battery assembled with Nafion 115 membrane and microporous membrane is about 1.9 V (1.6 V) and1.8 V (1.7 V), respectively. Further results obtained in terms of the analysis by testing software show that the CE of the batteries decreases from 98% to 83%, when porous membranes were used instead of Nafion 115. The difference is caused by the high diffusion rate of bromine through the microporous membrane compared to Nafion 115. Meanwhile, the voltage efficiency (VE) of this battery increases from 80% to 92% due to the

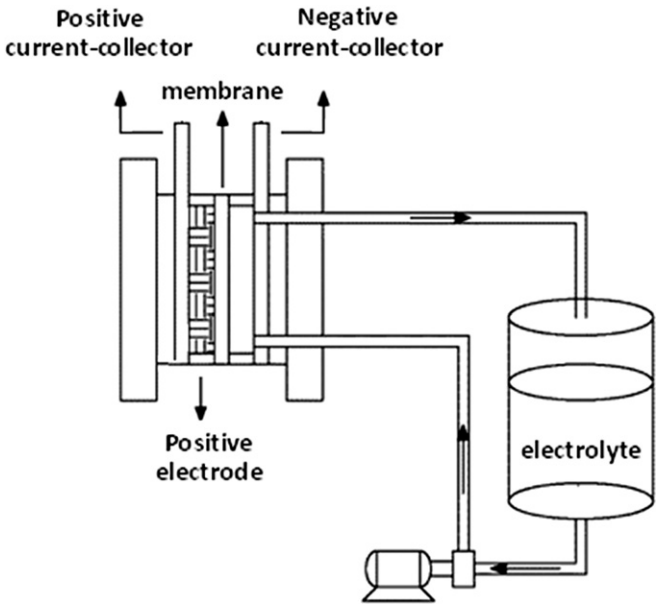

Fig. 1. Schematic diagram of a single flow zinc–bromine battery.

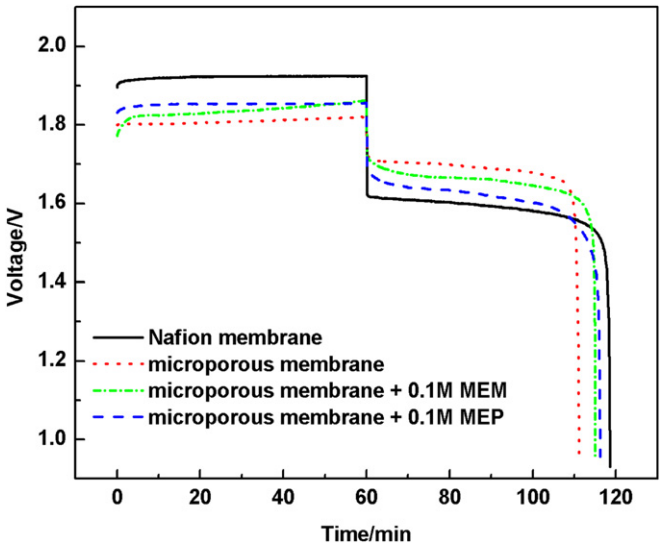

Fig. 2. Charge–discharge curves of single flow ZBB at room temperature under a constant current density of 20 mA cm^{-2}.

low ohmic resistance of microporous membrane compared to Nafion 115. To further decrease the cross-over of bromine through the microporous membranes, a complexation agent was added into the positive slurry. The results show that the CE of battery assembled with microporous membranes increases from around 89% to 93% and 92% when N-methyl-ethyl-pyrrolidinium (MEP) and N-methyl-ethyl-morpholinium (MEM) were added into positive side as complexation reagents. However, the average charge–discharge voltage and VE of battery decrease from around 92% to 86% and 89% respectively. Considering the much lower cost of Daramic microporous membranes, in this system, microporous membranes will be selected as separator, and MEP or MEM as complexation reagent.

Fig. 3 demonstrates a series of CVs recorded in the potential range of 0–1.2 V vs. SCE at the scan rate of 20 mV s^{-1}. As shown in Fig. 3(a) and (b), two very weak anodic and cathodic peaks exist in the electrolyte with 0.1 M MEM and 0.1 M MEP, which are attributed to the redox reactions of O_2. The results indicate that MEP and MEM are stable in potential range between 0 V and 1.2 V. The anodic and cathodic peaks from the curves in Fig. 3(c)–(e) result from the redox reaction of Br^-/Br_2. It can be seen that the cathodic peak current is much higher in curve Fig. 3(c) and (d) than that in curve Fig. 3 (e), which might be due to the aggregation of oxidation product (Br_2) on the electrode, implying that MEP and MEM can effectively complex with bromine. Meanwhile, the cathodic peak potentials shifted from about 610 mV to 560 mV and 480 mV (vs. SCE), respectively, when the MEP and MEM were added in the electrolytes. It is known that the energy density is based on the properties of active species employed in the positive and negative electrodes, such as, discharge voltage, electrochemical equivalent and concentration of active species dissolved in the electrolytes. The shift of cathodic peak potential would induce the lower discharge voltage and energy density [20]. To balance the CE and energy density of the positive redox couple, the MEM is preferred for use in the positive half-cell of single flow ZBB. As shown in Fig. 2, the EE of the single flow ZBB can reach 80% by using MEM as complexation reagent.

Fig. 4 shows the effect of current densities and capacities on the performance of battery. It can be seen that the average charge voltage increases, while the average discharge voltage decreases with increasing current density. The voltage of battery drastically

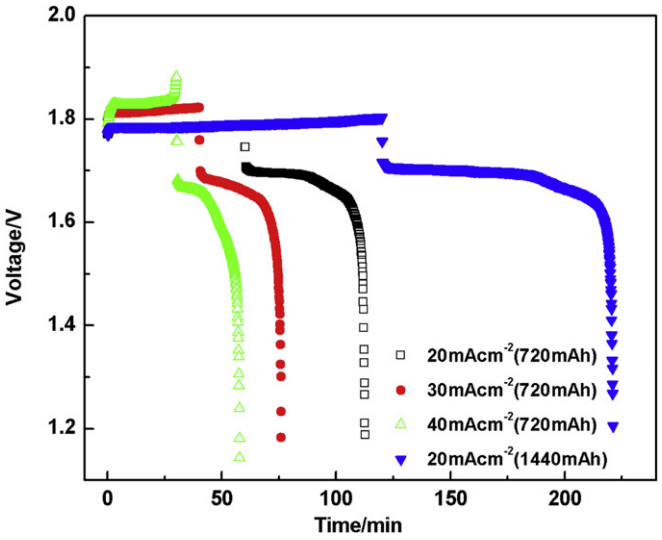

Fig. 4. Charge–discharge curves of single flow ZBB at room temperature under disparate constant current density and capacity.

increases at the end period of charging process at 40 mA cm^{-2}. This indicates that the high polarization was mainly attributed to the density polarization. Further results show that the VE of the single flow battery decreases from 88% to 87% while the EE decreases from 82% to 79% when the current density increases from 20 mA cm^{-2} to 40 mA cm^{-2}. The charge and discharge curves with fixed capacity in Fig. 4 reveal that the EE of single flow ZBB can reach 79% at the capacity 1440 mA h (charge time: 2 h), which is comparable with reported performances of traditional ZBB [11]; it however, has much lower weight and bromine emission.

The cycle life test was carried on the single flow ZBB to investigate its stability. The change of CE, VE and EE during charge–discharge cycles of the single flow ZBB, used microporous membrane and the 0.1 M MEM as separator and complexation reagents respectively was presented in Fig. 5. The performance of the battery kept very stable during 70 charge–discharge cycles.

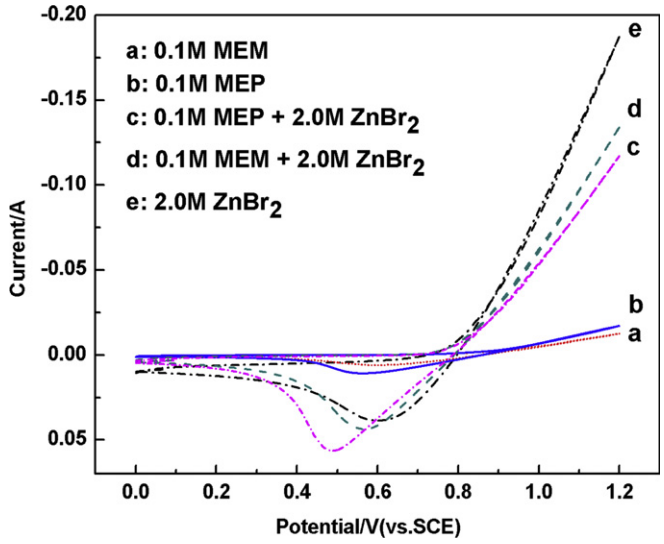

Fig. 3. CVs at 25 °C with a scan rate of 20 mV s^{-1} in electrolytes with 2.0 M Zn^{2+} and various complexation agents, pH = 3.

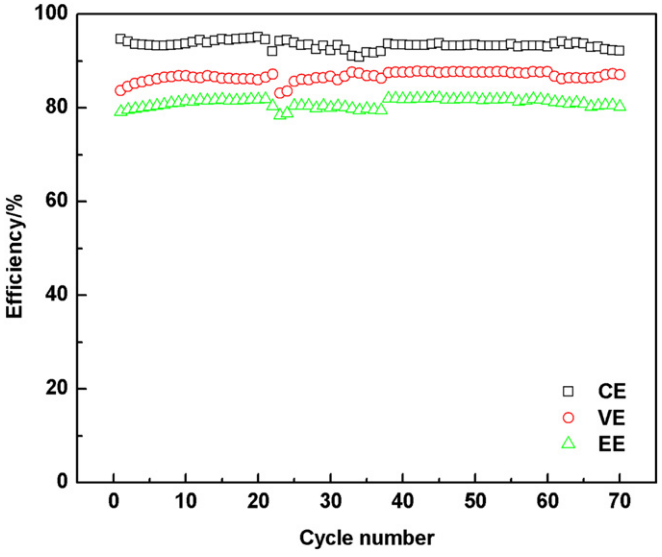

Fig. 5. The cycle life of the single flow ZBB. (The current density: 20 mA $cm^{-2}$and capacity: 720 mA h).

4. Conclusions

A novel single flow ZBB was designed and fabricated to improve the energy density of currently used ZBB. By using Daramic microporous membranes as separator, MEM as complexation reagents, the performance of designed battery can reach CE of 92%, EE of 82% when operating at the constant current density of 20 mA cm^{-2}, which is comparable with the traditional ZBB. However, the new battery design shows much lower weight or improved energy density than traditional ZBB, as well as much lower bromine emission. Therefore, the single flow ZBB is an attractive system being worthy to make great efforts to investigate deeply further.

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